Antimony in recent, ombrotrophic peat from Switzerland and Scotland: Comparison with natural background values (5,320 to 8,020 ^{14}C yr BP) and implications for the global atmospheric Sb cycle

William Shotyk, Michael Krachler, and Bin Chen

Institute of Environmental Geochemistry, University of Heidelberg, Heidelberg, Germany

Received 30 June 2003; revised 28 October 2003; accepted 21 November 2003; published 28 January 2004.

[1] The lowest concentrations, atmospheric fluxes, and enrichments of Sb in a Swiss bog were found in peat samples dating from 8,020 to 5,320 ^{14}C yr BP when Sb inputs were proportional to those of Sc and effectively controlled by deposition of soil dust. For comparison with these ancient samples, modern peat samples from five rural areas of Switzerland and two remote areas of Scotland and Shetland are highly contaminated with Sb, with enrichments of the order of 30 to 80 times. "Lithogenic" Sb concentrations calculated using the Sc concentrations and background Sb/Sc ratio are dwarfed at all sites by "anthropogenic" Sb. The chronology and intensity of the Sb enrichments are in many ways similar to those of Pb which indicates that (1) Sb, like Pb, is well preserved in ombrotrophic peat and (2) the extent of human impacts on the geochemical cycle of Sb is comparable to that of Pb. The similar distribution of Sb and Pb can be explained in terms of their chemical and mineralogical associations, with most lead minerals being rich in Sb. Assuming that the "background" Sb flux (0.35 μg/m^2/yr) from the Swiss bog is representative of preanthropogenic deposition rates worldwide, the global flux of natural Sb is estimated at 154 T/a. Using the natural Pb flux published by *Patterson and Settle* [1987] of 2600 T/a and the "background" Pb/Sb ratio (29) of the preanthropogenic peat samples, the global flux of natural Sb is estimated at 90 T/a. Either way, these values (90 to 154 T/a) are considerably lower than the current estimate of natural Sb to the global atmosphere (2400 T/a) published by *Pacyna and Pacyna* [2001]. Assuming that the current estimate of anthropogenic Sb to the global atmosphere (1600 T/a) is correct [*Pacyna and Pacyna*, 2001], the ratio of anthropogenic to natural Sb emissions is on the order of 10 to 18. Taken together, the data from modern and ancient peat samples suggests that the impact of human activities on the global geochemical cycle of Sb may have been underestimated by an order of magnitude. Like Pb, Sb has no known biological function, has a similar toxicity, and is a cumulative poison. The environmental geochemistry of Sb therefore may have a relevance to human and environmental health comparable to that of Pb. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0330 Atmospheric Composition and Structure: Geochemical cycles; *KEYWORDS:* geochemical cycle, antimony, lead, peat, ombrotrophic bog, human impacts

Citation: Shotyk, W., M. Krachler, and B. Chen (2004), Antimony in recent, ombrotrophic peat from Switzerland and Scotland: Comparison with natural background values (5,320 to 8,020 ^{14}C yr BP) and implications for the global atmospheric Sb cycle, *Global Biogeochem. Cycles*, *18*, GB1016, doi:10.1029/2003GB002113.

1. Introduction

[2] Antimony is a chalcophilic trace element which is found in practically all sulphide minerals [*Boyle and Jonasson*, 1984]. The principal ore mineral of antimony is stibnite, Sb_2S_3 and its first recorded use as a pigment to make mascara is mentioned in an Egyptian papyrus dating from 1600 B.C. According to *Emsley* [2001], the first uses of Sb are even more ancient, with part of a 5000 year old vase now in the Louvre made of almost pure Sb. Thus Sb has been used directly and indirectly by man for several thousand years. The environmental significance of Sb in many ways should be comparable to that of Pb: Sb has no known biological function, it is toxic to animals at comparable concentrations, and Sb too is a cumulative poison [*Emsley*, 2001]. Moreover, most lead minerals contain abundant Sb (Table 1). Thus there should exist a strong link between both the natural and the anthropogenic geochemical cycles of these two elements. Processes which

0886-6236/04/2003GB002113

Table 1. Concentrations of Sb in Some Lead Minerals (From *Nriagu* [1983])

Mineral Name	Mineral Formula	Antimony Concentration, %
Andorite	$PbSb_3S_6Ag$	41.8
Boulangerite	$Pb_2Sb_2S_5$	29.8
Bournonite	$PbSbS_3Cu$	24.9
Cylindrite	$Pb_3Sb_2S_{14}Sn_3$	13.6
Diaphorite	$Pb_2Sb_8SAg_3$	55.8
Fizelyte	$Pb_5Sb_8S_{18}Ag_2$	34.7
Franckeite	$Pb_5Sb_2S_{14}Sn_3$	11.7
Freieslebenite	$Pb_3Sb_5S_{12}Ag_5$	28.2
Geochronite	$Pb_5Sb_2As_2S_8$	23
Jamesonite	$Pb_4Sb_4S_{14}Fe$	35.4
Kobellite	$Pb_2Sb_2S_5Bi_2$	19.7
Meneghinite	$Pb_{13}Sb_7S_{24}Cu$	19.5
Nagyagite	$Pb_5Sb_4S_7AuTe_4$	19.8
Owyheeite	$Pb_5Sb_6S_{15}Ag_2$	29.6
Plagionite	$Pb_5Sb_8S_{17}$	38.1
Ramdohrite	$Pb_3Sb_6S_{13}Ag_2$	36.8
Selenokobellite	$Pb_2Sb_2S_5Bi_2Se_5$	14.9
Semseyite	$Pb_9Sb_8S_{21}$	27.7
Zinkenite	$Pb_6Sb_{14}S_{27}Fe$	44.7

release Pb to the environment such as metallurgical processing (especially lead refining) and coal burning therefore should also release considerable quantitites of Sb. Soils in the vicinity of lead smelters have been found to contain up to several thousand ppm Sb [*Kimbrough and Suffet*, 1995]. Copper ores also may contain significant quantities of Sb [*Bailey*, 1961], and soils in the vicinity of Cu smelters have been found to contain several hundred ppm of Sb [*Crecelius et al.*, 1974, 1975]. For comparison, the abundance of Sb in the Earth's crust is approximately 0.3 ppm [*Wedepohl*, 1995].

[3] In contrast to the anthropogenic geochemical cycle of Pb which is comparatively well understood [*Hutchinson and Meema*, 1987], far less is known about the environmental fate and significance of Sb [*Filella et al.*, 2002a, 2002b]. Compared to Pb, there have been far fewer studies of Sb in the environment [*Bodek et al.*, 1988; *Fowler and Goering*, 1991] and the impact of human activities on the geochemical cycle of Sb is poorly known. Unlike Pb, there are very few retrospective studies of the changing rates and sources of atmospheric Sb using archives such as polar snow and ice, lake sediments, or peat bogs.

[4] Concentrations of Sb have been measured in the surface peat layers of Norwegian bogs, and compared with Sb concentrations in peat deeper layers [*Hvatum*, 1983]. The main findings of that study were (1) Sb concentrations in the surface peat layers are considerably higher than in peat from deeper (50 cm) layers and (2) that Sb concentrations in the surface peat layers from bogs in southern Norway are approximately 10X greater than in the peat cores collected in northern Norway. These findings showed that the surface peat layers were impacted with Sb from human activities, with the south-north concentration gradient due to long-range atmospheric transport of Sb and other contaminants [*Steinnes*, 1987]. These studies employed radiochemical neutron activation analysis to measure Sb [*Njåstad et al.*, 1987], but the relatively high detection limit (60 ng/g) meant that Sb could not be quantified in the deeper peat layers from many sites [*Steinnes and Njåstad*, 1995]. In other words, these studies failed to accurately determine the "natural background" values for Sb, against which the concentration data from surface layers needs to be compared. Also, the Sb concentration data from the Norwegian bogs were not corrected for differences in natural abundance of mineral matter or extent of organic matter decay. Therefore it is not known to what extent the elevated Sb concentrations in the surface peat layers could be due to differences in the rates of dust deposition, peat growth rates, or humification of plant matter. In addition, these studies did not consider the possible importance of natural geochemical processes on the vertical distribution of Sb in the peat profiles. The Sb concentration data alone therefore has to be interpreted with care. Finally, the Norwegian peat cores were arbitrarily sectioned into relatively large depth increments (e.g., 3–5 cm, and 10, 20, and 50 cm) and were not age dated. Thus rapid changes in Sb deposition rates with respect to time would have been "smoothed" by averaging concentration changes over large depth increments, and these cores provide only a crude outline of possible changes in the atmospheric Sb deposition rates. Despite these shortcomings, the studies published to date remain valuable because they clearly show that Sb concentrations in modern moss and peat samples (up to 3 ppm Sb) are far greater than the samples from deeper, older peat layers (<0.06 ppm).

[5] A peat core from an ombrotrophic ("rain-fed") bog in the Jura Mountains of Switzerland, Etang de la Gruère (EGR), has provided a complete record of atmospheric Pb accumulation since 12,370 ^{14}C yr BP [*Shotyk et al.*, 1998]. In the peat samples from 12,370 to 3000 ^{14}C yr BP, Pb concentrations are proportional to those of Sc, a conservative lithogenic element which reflects the abundance of silicate dust supplied by weathering of rocks and soils [*Shotyk et al.*, 1998]. In addition, the isotopic composition of Pb in these preanthropogenic peats is similar to that of crustal rocks [*Shotyk et al.*, 2001]. Taken together, these data suggest that the Pb flux to peat dating from preanthropogenic times (i.e., older than 3000 ^{14}C yr BP) was proportional to that of atmospheric soil dust (ASD). Since 3000 ^{14}C yr BP, however, anthropogenic sources of Pb have dominated the Pb flux to the bog, and the chronology of these changes is discussed in detail elswhere [*Shotyk et al.*, 1998, 2001].

[6] Ombrotrophic bogs are excellent archives of atmospheric Pb deposition because they receive Pb only from the air [*Shotyk et al.*, 2001] and because they efficiently retain this metal despite the low pH of the waters (pH 4), the abundance of natural, complex-forming organic acids, and the seasonal variations in redox potential. Studies of the isotopic composition of Pb in cores dated using ^{210}Pb have shown that Pb is effectively immobile in peat profiles [*Shotyk et al.*, 1997; *Weiss et al.*, 1999a]. This interpretation has been confirmed using studies of the isotopic composition of Pb from herbarium specimens of *Sphagnum* moss [*Weiss et al.*, 1999b]. In addition, measurements of both the concentrations of individual alkylead species (originating in leaded gasoline) with the isotopic composition of Pb in a

peat core dated with ^{210}Pb lends further support to the view that peat cores from ombrotrophic bogs yield highly reproducible Pb chronologies [*Shotyk et al.*, 2002a]. Finally, independent investigations by other workers in this field have come to the same conclusion about Pb [*Vile et al.*, 1995, 1999; *Bränvall et al.*, 1997; *Farmer et al.*, 1997; *Kempter et al.*, 1997; *Martinez-Cortizas et al.*, 1997; *MacKenzie et al.*, 1997, 1998; *Norton et al.*, 1997].

[7] Antimony was measured in the peat core from EGR using INAA, and these analyses showed that the chronology of Sb accumulation since the Roman Period was similar to that of Pb [*Shotyk et al.*, 1996]. The similar distribution of Sb and Pb argues that Sb, like Pb, is effectively immobile in ombrotrophic peat bog profiles. With respect to the deeper, preanthropogenic peat samples, Sb concentration measurements obtained using INAA (the most commonly used technique for this element) were found to lack sufficient sensitivity to measure Sb accurately. Taking 300 ng/g as the abundance of Sb in the Earth's crust and assuming there is no fractionation during chemical weathering, uncontaminated ombrotrophic peat containing 1% by weight mineral matter should contain on the order of 3 ng/g Sb; not many laboratories are capable of measuring Sb reliably in peat at these concentrations. Only recently, first using hydride generation atomic absorption spectrometry [*Krachler et al.*, 2001], then using ICP-Q-MS and ICP-SF-MS [*Krachler et al.*, 2002a], has it become possible to reliably measure Sb in peat at the very low concentrations (ng/g) which are characteristic of ombrotrophic peat dating from preanthropogenic times. Using these new analytical procedures to measure Sb in the peat bog profile at EGR has provided a record of atmospheric Sb deposition since 12,370 ^{14}C yr BP [*Shotyk et al.*, 2002b]. As is true of Pb, the lowest Sb concentrations were found in preanthropogenic peats dating from the Holocene climate optimum (5320 to 8020 ^{14}C yr BP) when dust fluxes were at their lowest and Sb concentrations averaged only 8 ± 3 ng/g (n = 17).

[8] For comparison with these background values, here we present new Sb and Sc concentration data for peat cores from five Swiss peatlands representing up to 3000 years of atmospheric Sb deposition. We show that the distribution and chronology of Sb in these peat profiles resembles that of Pb which supports the argument that Sb is effectively immobile in peat bogs. In addition, the enrichments of Sb in these peat cores are compared with the natural "background" Sb/Sc values from EGR to estimate the extent of human impacts. For comparison with these central European sites, we also present new Sb and Sc concentration data from peat bogs in NW Scotland and the Shetland Islands. The Sb concentration data for the Scottish peat cores was obtained using a new analytical procedure employing hydride-generation atomic fluorescence spectrometry (HG-AFS) which provides a detection limits for Sb in peat of only 2 ng/g [*Chen et al.*, 2003]. We show that the chronology of Sb contamination in Scotland is similar to that of Pb. Also, the extent to which Sb has been impacted by human activities is similar to that seen in Switzerland, even though the Scottish sites are much further from known emission sources. These new results suggest that the extent and intensity of human impacts on the global geochemical cycle of Sb may be comparable to that of Pb.

2. Materials and Methods

2.1. Sites Selected for Study

[9] A complete vertical peat profile from Etang de la Gruère (EGR) has been described in previous publications [*Shotyk et al.*, 2001]. The total length of the core was approximately 650 cm and represents approximately 14,500 calendar years of peat accumulation. The top 100 cm of the bog was collected using a Wardenaar corer (2F) and all subsequent samples removed using a Belarus corer (2P).

[10] For comparison with the data from the long core at EGR, two additional Wardenaar peat cores (ca. 10 × 10 × 100 cm) were collected in the Jura Mountains of Switzerland at La Tourbière des Genevez (TGE) and Praz Rodet (PRD); a fourth core was collected in the Alps at Suossa (SUO) in Canton Graubunden, and a fifth core from a minerotrophic fen, Gola di Lago (GDL) on the south side of the Alps in Canton Ticino. These peatlands have been briefly described elsewhere [*Shotyk et al.*, 2000].

[11] To compare with the Swiss peat cores, Wardenaar cores were also collected from a blanket bog in a remote part of the far northwest of Scotland at Loch Laxford (LL), and also at Fleck's Loch (FL) on the Island of Foula. Foula (population 36) is only ca. 6 km^2 and lies 30 km west of the main island ("mainland") of the Shetland Islands. These sites were described in a previous publication [*Shotyk*, 1997].

2.2. Sample Preparation

[12] All of the Wardenaar cores were cut by hand (using a stainless steel bread knife) into 3 cm slices. The peats below 100 cm at EGR were cored with a Belorussian peat sampler which removes semicylindrical cores 50 cm long and 10 cm in diameter; these core sections were cut into 10 cm slices. All peat samples were dried at 105°C in acid-washed Teflon bowls and macerated in a centrifugal mill equipped with a Ti rotor and 0.25 mm Ti sieve (Ultracentrifugal Mill ZM 1-T, F. K. Retsch GmbH and Co., Haan, Germany). The milling was carried out in a Class 100 laminar flow clean air cabinet to prevent possible contamination of the peat samples by lab dust.

2.3. Chemical Analyses

[13] Scandium and Sb concentrations were measured in all samples using INAA analyses of bulk powders. Antimony was also measured in the peat profile from EGR using HG-AAS following acid digestion [*Krachler et al.*, 2001] and these data were also published earlier [*Shotyk et al.*, 2002b]. The Sb concentrations obtained using HG-AAS [*Krachler et al.*, 2001] are in good agreement with previous values obtained using INAA [*Shotyk et al.*, 1996] for the 2F peat core and are also in good agreement with values obtained for both peat cores (2F and 2P) using ICP-Q-MS [*Krachler et al.*, 2002a]. Here, the INAA data for the EGR 2F core are presented, only because the data set is more complete (some of the samples had already been used up by the time Sb was measured using HG-AAS). With respect to the 2P core (deeper, older peat layers), the HG-AAS data is

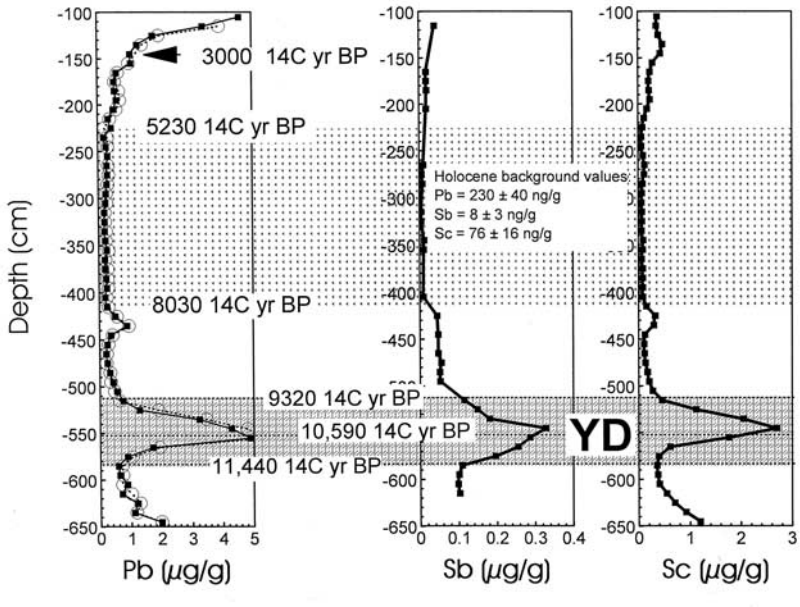

Figure 1. Concentrations (μg/g) of Pb, Sb, and Sc in the 2P core from EGR. The Sb and Sc data are from *Shotyk et al.* [2002b]. The Pb data (hollow circles) is either from *Shotyk et al.* [1998] or represents new, unpublished data (solid squares). The average concentrations from 5230 to 8030 ^{14}C yr BP (natural background values) are (ng/g) 230 Pb, 8 Sb, 76 Sc.

presented here because it is much more accurate than the INAA data at low Sb concentrations. Antimony was measured in the two peat cores from Scotland using HG-AFS as described in detail by *Chen et al.* [2003].

[14] All of the Pb concentration data presented here for the Wardenaar peat cores have already been published [*Shotyk*, 1996; *Shotyk et al.*, 2000] and was obtained using the EMMA XRF [*Cheburkin and Shotyk*, 1996]. The Pb concentrations in the 2P core from EGR are a new set of measurements obtained using the digestion procedure and ICP-Q-MS protocol described elsewhere [*Krachler et al.*, 2002b]. These new Pb concentration measurements are consistent with those published previously [*Shotyk et al.*, 1998, 2001] as seen in Figure 1. The "natural background" Pb concentrations previously reported for this peat bog profile [*Shotyk et al.*, 1998, 2001] in peat samples dating from 5320 to 8020 ^{14}C yr BP are 277 ± 39 ng/g (n = 18) which is consistent with the new results presented here (230 ± 40 ng/g, n = 18).

2.4. Radiometric Age Dating

[15] All of the ^{14}C age dates presented here are taken from previous publications. Age dating of the Wardenaar cores using ^{210}Pb (CRS model) has already been published for some of the cores, e.g., EGR, TGE, PRD [*Appleby et al.*, 1997]. The ^{210}Pb chronologies for SUO, GDL, LL, and FL have not been published, and here only selected ^{210}Pb ages are presented.

3. Results

3.1. Natural Background Concentrations and Fluxes of Pb

[16] The concentrations of Pb were proportional to those of Sc from 12,370 ^{14}C (when peat formation began) to 3000 ^{14}C yr BP (Figure 1). Because Sc is a conservative, lithogenic element, it serves as a surrogate for the abundance of atmospheric soil dust (ASD) delivered to the bog surface [*Shotyk et al.*, 2001]. The correlation between Pb and Sc shows that the Pb fluxes were controlled and regulated by the fluxes of ASD. Twenty-eight ^{14}C age dates for the 2F and 2P profiles yielded an average peat accumulation of 0.45 mm/a, allowing the atmospheric fluxes to be calculated for the elements of interest. The lowest Pb concentrations (230 ± 40 ng/g) and the lowest rates of atmospheric Pb deposition (10 μg/m^2/yr Pb) are found in the peats dating from 5320 to 8020 ^{14}C yr BP: This corresponds to the Holocene Climate Optimum (HCO) when vegetation cover was at its greatest extent, and the fluxes of ASD were at their lowest.

3.2. Natural Background Concentrations and Fluxes of Sb

[17] The average Sb concentration (obtained using ICP-MS) for peats dating from 5320 to 8020 ^{14}C yr BP is 8 ± 3 ng/g (n = 8) and is proportional to that of Sc (Figure 1). The average Pb/Sb ratio (28.8) of these samples implies that the pre-anthropogenic Sb flux was 10/28.8 = 0.35 μg/m^2/yr. Thus this section of the EGR peat profile provides the first estimated "natural background" rate of atmospheric Sb deposition for this part of Europe. We are not aware of any other reports of "background" rates of atmospheric Sb deposition for any other regions.

3.3. Sb in Recent Peat Samples From Switzerland and Comparison With Sc and Pb

[18] In the deeper layers from all of the Swiss peat cores, Sc concentrations exceed those of Sb (Figure 2) whereas in

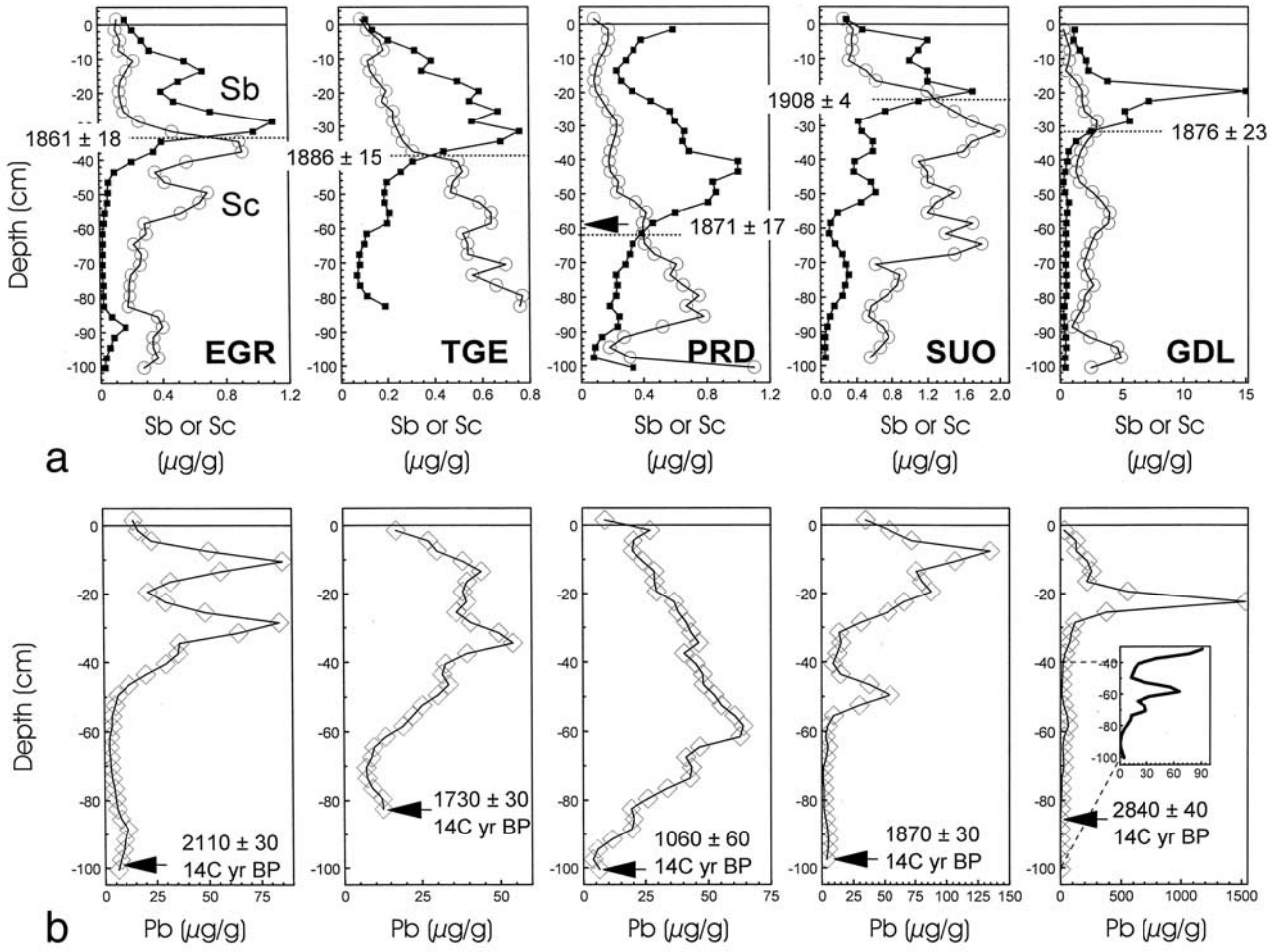

Figure 2. (a) Sb or Sc concentrations (μg/g) in the peat profiles from EGR, TGE, PRD, SUO, and GDL. (b) Pb concentrations (μg/g) for the same profiles. The ^{14}C age dates shown represent the age of the last sample of each of these Wardenaar peat cores.

the uppermost, recent peat layers, it is the other way around. Each of these cores has a unique age-depth relationship, reflecting such factors as the climate-dependent differences in rates of peat accumulation. Thus differences between the cores in the relative abundance of Sb with depth do not necessarily represent different Sb chronologies. To compare the relative changes in Sb and Sc, a horizontal line has been drawn at the depth where [Sb] = [Sc]. Because the natural ratio of Sb to Sc is 8 ng/g to 76 ng/g (Figure 1), the depth where [Sb] = [Sc] represents an enrichment in Sb, relative to the natural background value, of approximately a factor of 10. Using the ^{210}Pb chronologies, the ^{210}Pb ages for these lines are also indicated. In the case of PRD where the ^{210}Pb ages do not extend sufficiently deep into the profile, the position of the nearest sample which could be dated using ^{210}Pb is indicated by the arrow. The data shown in Figure 2 indicate that the point at which [Sb] = [Sc] is variable with respect to depth but similar with respect to time at all sites. For example, at PRD the depth at which [Sb] = [Sc] is found at a depth of 62 cm, but in the SUO core, at 22 cm (Figure 2). Despite the relatively large difference in the depth of this feature between the two cores (40 cm), the age dates are similar: Between the end of the 19th century at GDL and the beginning of the 20th century at SUO. Given the accuracy of the ^{210}Pb age dating (ca. ± 10 years for samples which are ca. 100 years old) and the thickness of the peat slices (3 cm), these are very similar chronologies. In the other Swiss cores, this feature ([Sb] = [Sc]) is found at intermediate depths and date from the end of the 19th century (Figure 2). It is most unlikely that the variations in Sb concentrations with respect to depth are caused by internal, geochemical processes operating within the peatlands because four of the five peatlands (EGR, TGE, PRD, and SUO) are ombrotrophic bogs which have very similar chemical properties, at least in the surface layers. If geochemical processes were responsible for the vertical distribution of Sb, the variation in Sb concentration with depth should be very similar at these four sites. Moreover, the chronologies of Sb accumulation are very similar in these cores (Figure 2). The similar Sb chronologies therefore must

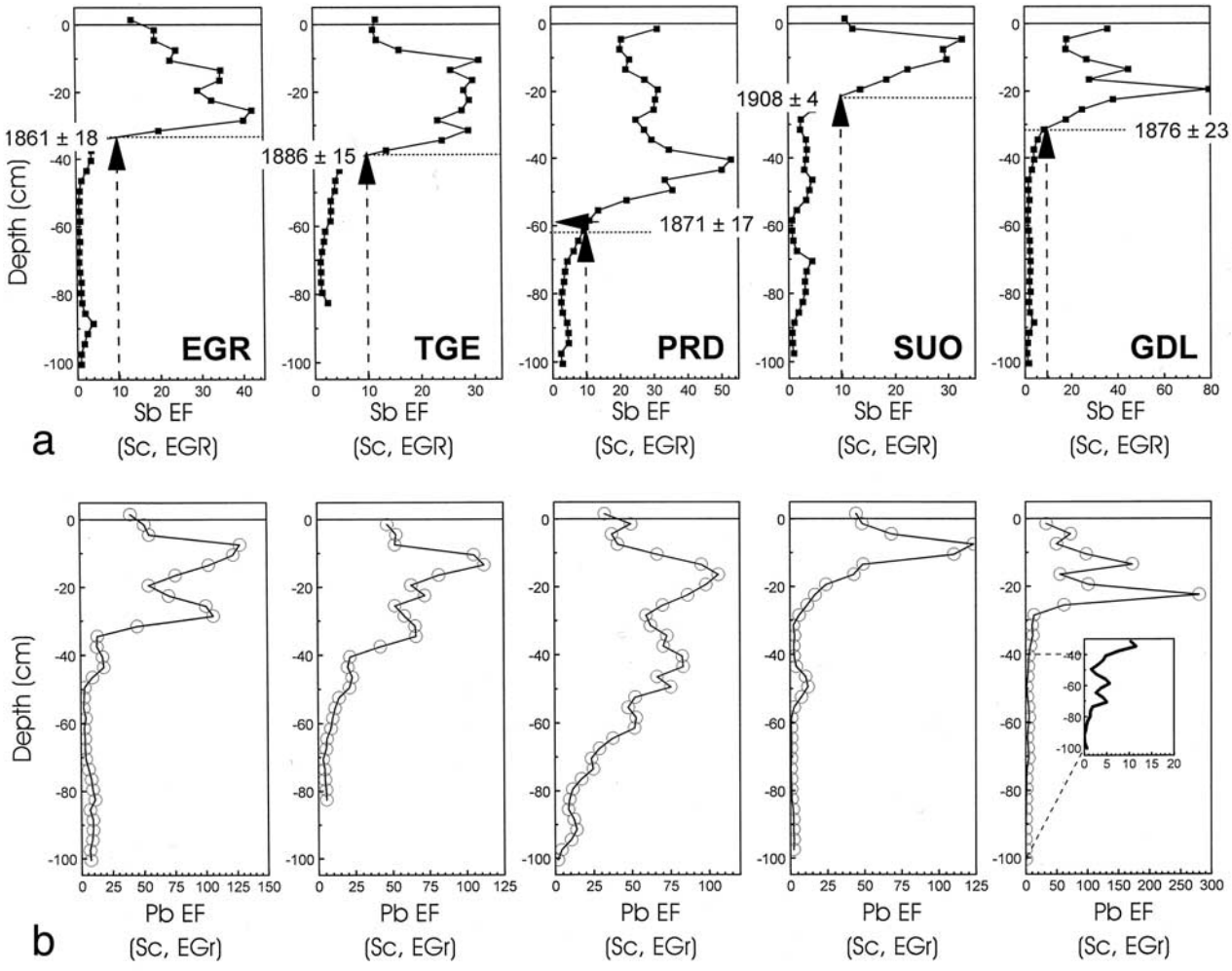

Figure 3. (a) Sb EF (number of times) calculated using the "natural background" Sb/Sc ratio (8/76) of the preanthropogenic peat samples from EGR for the Wardenaar peat cores from EGR, TGE, PRD, SUO, and GDL. The horizontal dotted line indicates the depth at which Sb EF = 10. Notice that this point is found at varying depths in the different peatlands but is similar in age. (b) Pb EF (number of times) calculated using the "natural background" Pb/Sc ratio (230/76) of the preanthropogenic peat samples from EGR.

have been caused by processes external to the peatlands related to the changing rates of atmospheric Sb deposition.

[19] Total concentrations of Pb are also shown in Figure 2, for comparison with Sb. Notice that the distribution of Sb is independent of Sc (which reflects the abundance of mineral matter), but rather similar to that of Pb (which has been derived predominately from anthropogenic sources for two to three thousand years).

3.4. Enrichments of Sb in Recent Peat From Switzerland

[20] Now that accurate, precise measurements of Sb have been obtained for the pre-anthropogenic section of the EGR core [*Shotyk et al.*, 2002a] using HG-AAS [*Krachler et al.*, 2001] and confirmed using ICP-MS [*Krachler et al.*, 2002a], the "natural background" Sb concentrations (8 ng/g) and Sb/Sc ratio (0.105) have been established. Using this value ("background" Sb/Sc at EGR), a realistic Sb enrichment factor (EF) can be calculated for the recent peat samples from EGR and the other Swiss cores (Figure 3). The Sb EF is calculated as the ratio

$$\text{Sb EF}_{\text{EGR}} = \left([\text{Sb}]/[\text{Sc}]_{\text{sample}}\right)/([\text{Sb}]/[\text{Sc}])_{\text{backgrounnd, EGR}}$$

and this data shows that Sb is significantly enriched in all peat samples which have accumulated since the Roman Period. Relative to pre-anthropogenic peats, a tenfold enrichment of Sb is seen in all of the peat cores by the end of the 19th century (Figure 3). The maximum Sb EF values are in the range 31 to 80X, which represents a substantial enrichment, compared with preanthropogenic samples.

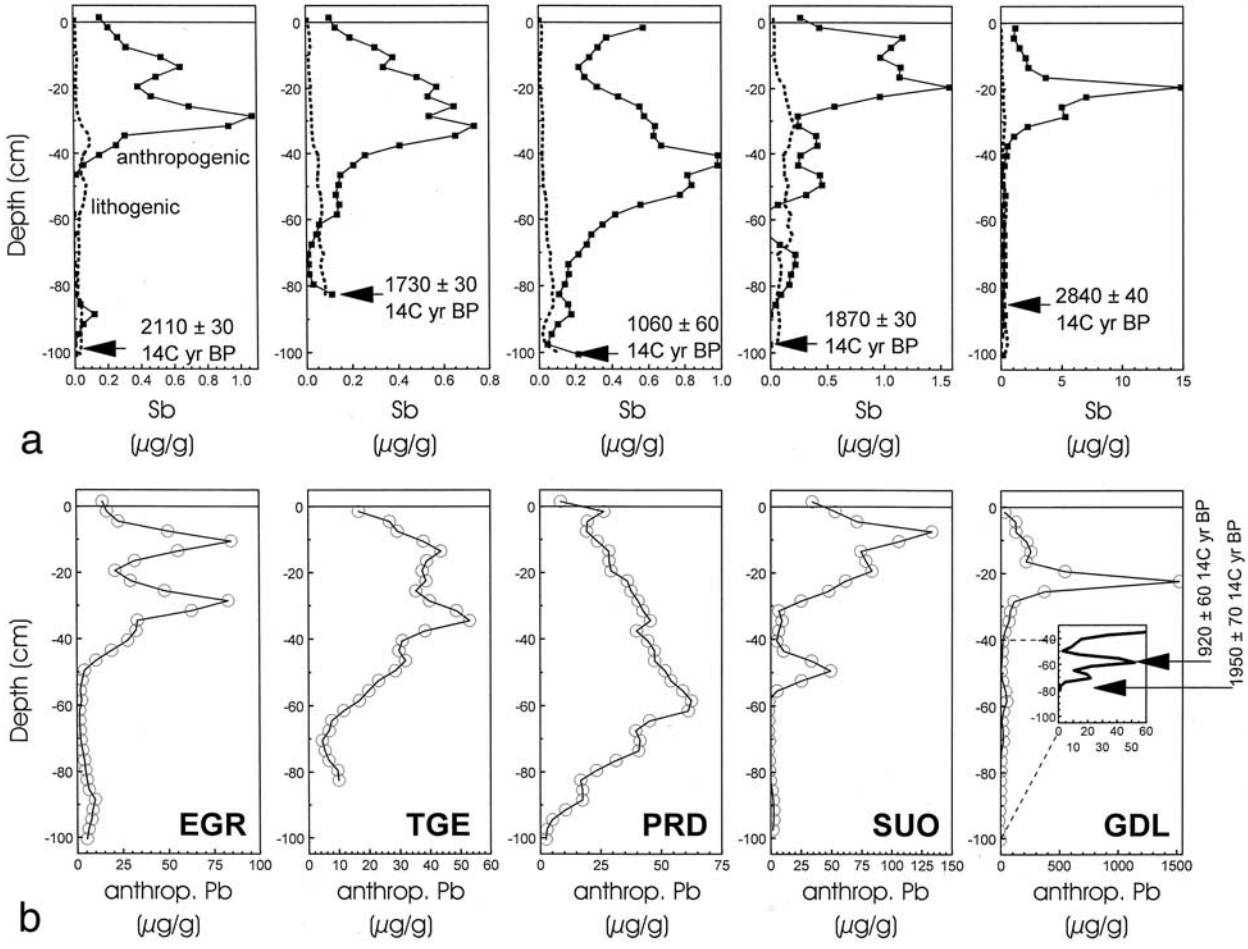

Figure 4. (a) Lithogenic and anthropogenic Sb concentrations calculated as described in the text for the Wardenaar peat cores from EGR, TGE, PRD, SUO, and GDL. (b) Lithogenic and anthropogenic Pb concentrations calculated as described in the text.

[21] The Sb EF profiles have many features in common with the Pb EF profiles (Figure 3). In general, the maximum Pb EF values exceed the maximum Sb EF values by ca. 2 to 4 times. The greatest enrichments of Sb and Pb are seen in the fen peats from Gola di Lago where the EF values reach 79 and 280X, respectively (Figure 3). While this peat profile is certainly minerotrophic [*Shotyk*, 1996], the vertical distribution of Sb concentrations and EF shows that the inputs of Sb, like those of Pb [*Shotyk*, 2001], have been predominantly, if not exclusively, atmospheric. The anomalous Sb and Pb EFs in the GDL core reflect its situation on the south side of the Alps where it is in direct contact with air masses influenced by the heavily industrialised region of northern Italy.

[22] To further emphasise the predominance of anthropogenic contributions to the Sb inventories in these cores, Sb from lithogenic sources has been calculated using the Sc concentrations and the background Sb/Sc ratio:

$$[\mathrm{Sb}]_{\mathrm{lithogenic}} = [\mathrm{Sc}]_{\mathrm{sample}} \times (\mathrm{Sb}/\mathrm{Sc})_{\mathrm{background,\,EGR}}$$

"Anthropogenic Sb" was then calculated as the difference between total Sb and lithogenic Sb:

$$[\mathrm{Sb}]_{\mathrm{anthropogenic}} = [\mathrm{Sb}]_{\mathrm{total}} - [\mathrm{Sb}]_{\mathrm{lithogenic}}$$

In each of the Swiss peat cores, it is clear that lithogenic Sb is dwarfed by anthropogenic Sb at all sites (Figure 4). Also, the distribution of anthropogenic Sb is similar to that of anthropogenic Pb (Figure 4).

3.5. Enrichment of Sb in Recent Peat From NW Scotland and the Shetland Islands

[23] For comparison with the peat cores from Switzerland in the heart of central Europe, Sb and Sc were measured in peat cores from Loch Laxford in NW Scotland, and from Fleck's Loch on the Island of Foula in Shetland, both of which are remote from any industrial activities. Despite their locations, these profiles also reveal Sb concentrations in the uppermost layers which are in excess of the Sc concentrations (Figure 5). Again, a horizontal line indicates the depth at which [Sb] = [Sc]. The ^{210}Pb age dates

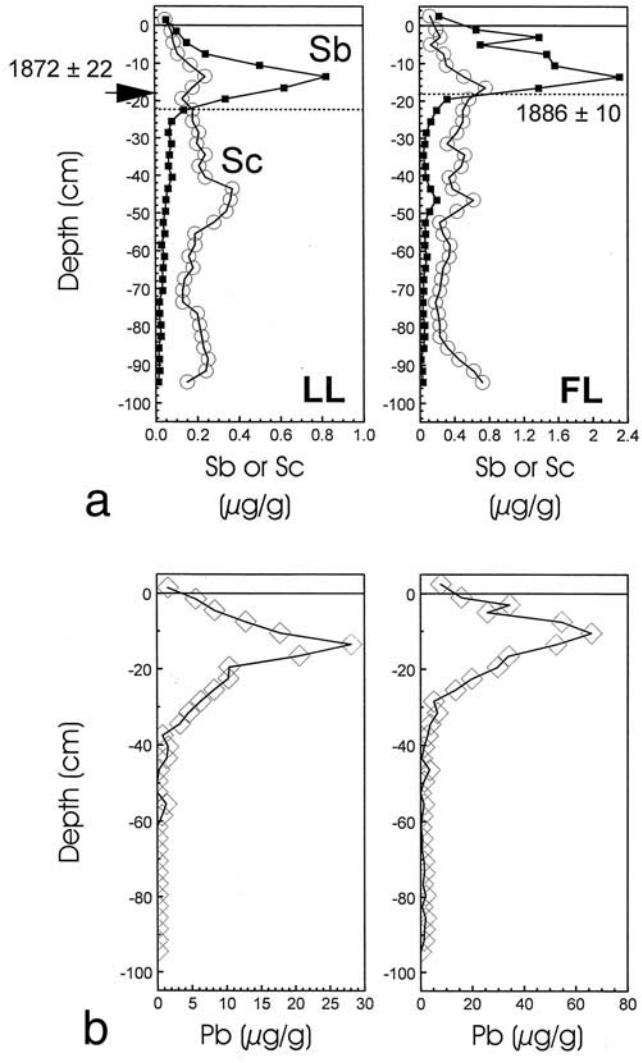

Figure 5. (a) Sb or Sc concentrations (μg/g) in the peat profiles from LL and FL. Acid digests were measured twice using HG-AFS [*Chen et al.*, 2003] and the results averaged. (b) Pb concentrations (μg/g) for the same profiles.

(W. Shotyk, unpublished data, 2003) show that this point which corresponds to a tenfold enrichment in Sb, relative to the background values established at EGR, also dates from the latter part of the 19th century. Therefore despite their remote locations, these sites reveal Sb concentrations and chronological changes in Sb/Sc which are comparable to those of the peat cores from Switzerland. Lead was also measured in the Scottish cores using XRF and again, the distribution of Sb is similar to that of Pb (Figure 5).

[24] To emphasise the anthropogenic Sb contributions to the Scottish peat cores, the Sb EFs were calculated using the background Sb/Sc from EGR. Again, the chronology of changes in Sb EF (Figure 6) is similar to that of Pb at both sites, and also similar to Sb EF profiles from the Swiss sites.

[25] Using the approach described earlier, Sb concentrations were separated into lithogenic and anthropogenic components (Figure 7). In both of the Scottish peat cores, anthropogenic Sb dominates the Sb inventories by a wide margin. Again, the distribution of anthropogenic Sb is similar to that of anthropogenic Pb.

[26] The Sb EF values in the Scottish peat cores are similar to those of the Swiss cores from the Jura and the Alps. Moreoever, in the Scottish cores the Sb EF values are comparable in magnitude to the Pb EF (Figure 6). In contrast, in the Swiss cores Sb EF values are approximately one-third to one-quarter of the Pb EF values (Figure 3). In other words, in the Scottish cores, the relative importance of

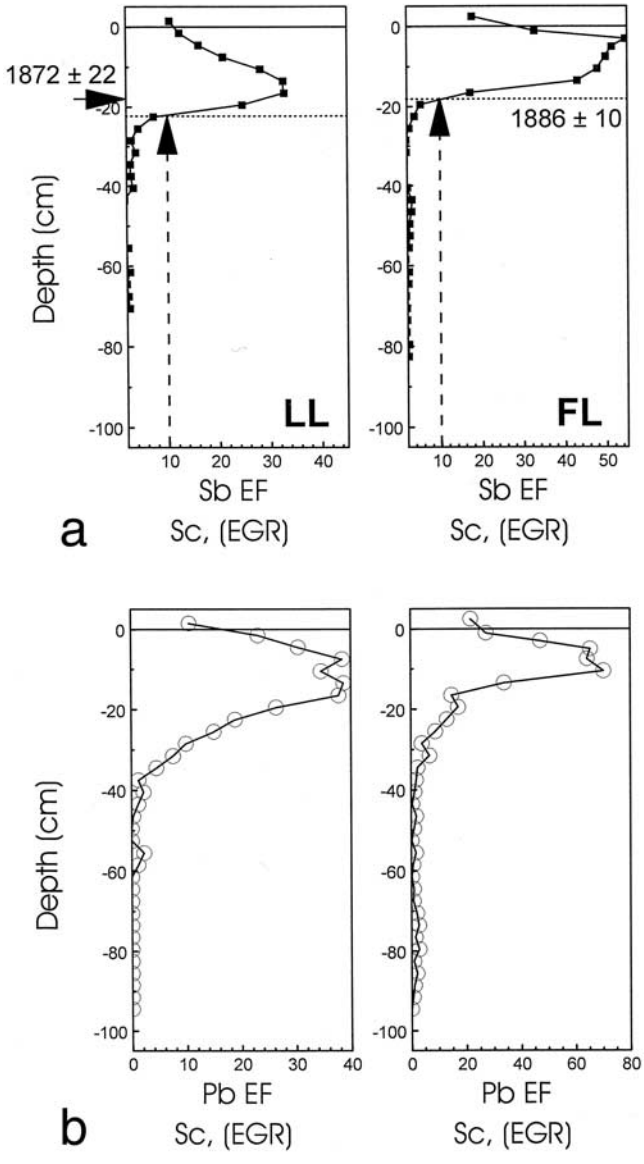

Figure 6. (a) Sb EF (number of times) calculated using the "natural background" Sb/Sc ratio (8/76) of the preanthropogenic peat samples from EGR for the Wardenaar peat cores from LL and FL. The horizontal dotted line indicates the depth at which Sb EF = 10. Notice that this point is similar in age to the corresponding point in the Swiss peat cores (Figure 3). (b) Pb EF (number of times) calculated using the "natural background" Pb/Sc ratio (230/76) of the preanthropogenic peat samples from EGR.

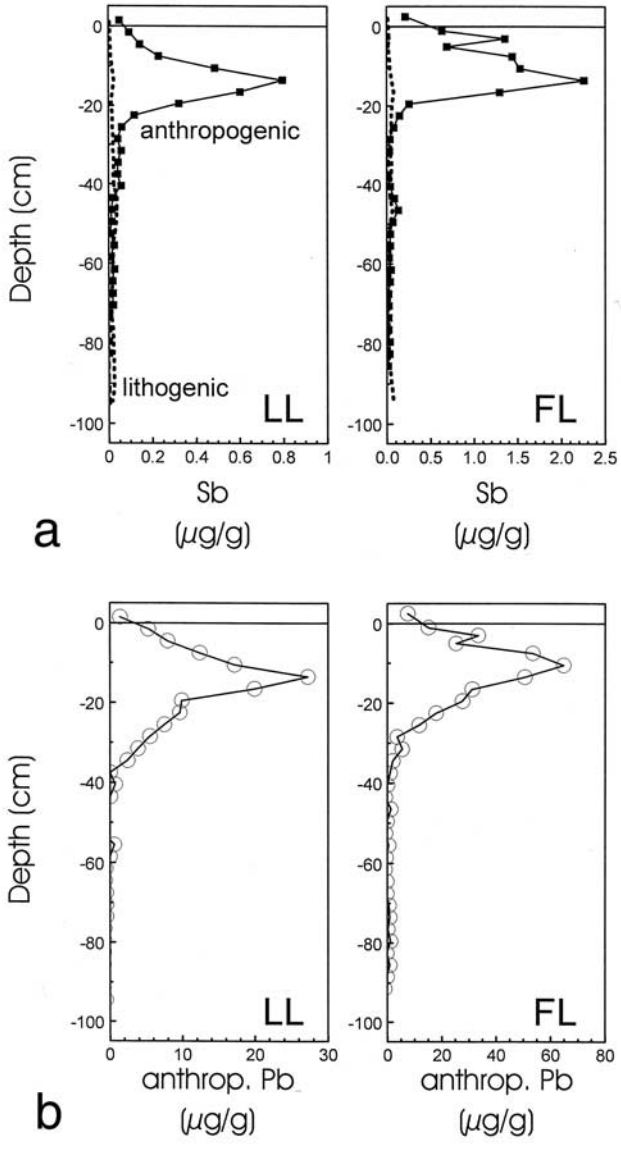

Figure 7. (a) Lithogenic and anthropogenic Sb concentrations calculated as described in the text for the Wardenaar peat cores from LL and FL. (b) Lithogenic and anthropogenic Pb concentrations calculated as described in the text.

Sb as a contaminant is comparable to that of Pb. For comparison, the cumulative deposition of anthropogenic Pb in the Swiss cores north of the Alps is ca. 2 g/m^2 [*Shotyk et al.*, 2000], compared with 1g/m^2 for the Scottish cores (W. Shotyk, unpublished data, 2003). Therefore the relative importance of anthropogenic Sb compared with Pb in Scotland partly reflects the greater inputs of anthropogenic Pb to the Swiss sites.

4. Discussion

4.1. Preanthropogenic Flux of Pb to the Global Atmosphere

[27] The existing data from EGR [*Shotyk et al.*, 2002b] provides measurements of Sb, Sc, and Pb concentrations in peat which has been accumulating since 12,370 ^{14}C yr BP. The lowest Pb concentrations are found in the samples dating from 5320 to 8230 ^{14}C yr BP. This period is characterised by the lowest fluxes of atmospheric soil dust since the Late Glacial [*Shotyk et al.*, 2002b] and corresponds to the Holocene Climate Optimum when vegetation cover was at its greatest extent. The relationship between the Pb and Sc concentrations suggests that atmospheric soil dust was the single most important control on atmospheric Pb deposition [*Shotyk et al.*, 2001]. Because these samples date from preanthropogenic times, they can be used as a point of reference against which modern samples of moss or peat may be compared. Therefore the Pb and Sc concentrations, EFs, and accumulation rates derived from this section of the bog are taken to represent the ''natural background'' values for this region.

[28] If the dust flux recorded by the peat bog at EGR is comparable to the dust deposition rates on other continents, and if the atmospheric Pb flux is controlled by the soil dust flux in these other areas, then the pre-anthropogenic Pb flux at EGR may be representative of the natural Pb fluxes on other continents. Taking the background Pb flux at EGR (10 µg/m^2/a) and extrapolating to the continental land area (147×10^6 km^2), we obtain an estimated natural flux of 1480 T/a Pb to the continents. If the natural flux of Pb to the oceans is comparable to the continental flux, then the total natural flux to the global atmosphere is ca. $3 \times 1480 = 4440$ T/a. This estimate is in good agreement with the natural Pb flux estimated by Patterson (2600 T/a), suggesting that the approach is a reasonable approximation of the global atmospheric Pb deposition rates. Our result, however, and that of *Patterson and Settle* [1987], contrasts with the current estimated flux of natural Pb to the global atmosphere (12,000 T/a) published by *Pacyna and Pacyna* [2001]. In other words, the current estimated flux of natural Pb to the global atmosphere [*Pacyna and Pacyna*, 2001] may be overestimated.

4.2. Preanthropogenic Flux of Sb to the Global Atmosphere

[29] Like Pb, the lowest Sb concentrations are found in the samples dating from 5320 to 8020 ^{14}C yr BP when soil dust fluxes were at their lowest. Moreover, the relationship between the Sb concentrations and the dust flux suggests that atmospheric soil dust was the single most important control on atmospheric Sb deposition. Again, because these samples date from preanthropogenic times, they can be used as a point of reference against which modern samples of moss or peat may be compared. Therefore the Sb concentrations, EFs, and accumulation rates derived from this section of the bog are taken to represent the ''natural background'' values for this region. In contrast to Pb, however, the peat samples from deeper, older layers (i.e., predating 8020 ^{14}C yr BP) contain a contribution to the Sb inventory from mineral weathering reactions at the peat-sediment interface; this is clearly seen in the Sb/Sc and Sb/Pb profiles which are described elsewhere [*Shotyk et al.*, 2002b]. As a result, the atmospheric Sb inventory is masked by diagenetic Sb in these deeper, minerotrophic layers. The peat bog at EGR therefore can only be used to reconstruct

Table 2. Concentrations (ng g^{-1} dry mass) of Sb in Virgin Elder Leaves Collected in Autumn 1998 at Different Locations in Germany

Location	N[a]	Concentration ± s	RSD, %
Directly beside motorway A	4	589 ± 30	5.1
50 m from motorway A	3	207 ± 13	6.3
Directly beside motorway B, height fraction 80 to 200 cm	4	591 ± 26	4.4
Directly beside motorway B, height fraction >200 cm	5	468 ± 19	4.1
Residential area 1	4	198 ± 9	4.5
Residential area 2	4	153 ± 5	3.3
Argentina, urban area	9	5.2 ± 0.3	5.8

[a]Number of subsamples analyzed.

the changing rates of atmospheric Sb deposition as far back in time as 8020 ^{14}C yr BP.

[30] Assuming that the natural Sb flux at EGR (0.35 μg/m^2/a) is also representative of the continental land mass (147×10^6 km^2) and extrapolating to the Earth's land area, we estimate that 51.4 T/a Sb is deposited by natural sources to the continental land mass, or 154.2 T/a Sb to the global atmosphere. Alternatively, using the estimated global Pb flux published by *Patterson and Settle* [1987] of 2600 T/a and the "background" Pb/Sb ratio of the preanthropogenic peat samples (230/8), the global flux of natural Sb is estimated at 90 T/a. Therefore the natural flux of Sb to the global atmosphere lies in the range 90 to 150 T/a. In contrast, the estimate of natural Sb to the global atmosphere published by *Nriagu* [1990] is 2600 T/a, and the more recent estimate published by *Pacyna and Pacyna* [2001] is 2400 T/a: These values now appear to be too high.

[31] If the natural Sb concentrations and fluxes recorded by the peat bog profile at EGR are applicable to the continental land mass, then the natural fluxes of Sb to the global atmosphere have been overestimated by a considerable margin. Also, if the estimated fluxes of anthropogenic Sb to the global atmosphere are correct, then the impact of human activities on the global cycle of Sb has been underestimated to a large extent. Antimony concentrations and atmospheric deposition rates should be obtained from ombrotrophic peat bogs on other continents as soon as possible, to help quantify both the natural and anthropogenic fluxes of atmospheric Sb.

4.3. Anthropogenic Enrichments of Sb in Swiss Peat Cores

[32] It is not possible that the Sb EF profiles in modern peats shown here could have been caused by changes in peat accumulation rates, as any change in this parameter would have affected Sb and Sc to the same extent. Also, the Sb EF profiles cannot be explained by chemical diagenesis, because the similarity of the Sb and Pb concentration profiles (*Shotyk et al.* [1996] and this paper) suggest that Sb, like Pb, is immobile in peat. Moreover, in spite of the great differences in the distribution of Sb enrichments with depth, their distribution with time is similar in all of the peat cores.

[33] The "natural background" Sb/Sc ratio in the peats from EGR on average are ca. fivefold greater than the corresponding Sb/Sc values of the Earth's crust [*Wedepohl*, 1995]. Lead has been enriched in these samples, relative to the UCC, to the same extent [*Shotyk et al.*, 1998, 2001]. Thus Sb, like Pb, is naturally enriched in atmospheric aerosols deposited during the Holocene Climate Optimum (HCO), relative to crustal abundance. This elevated EF may reflect the natural enrichment of Sb and Pb in the fine fraction of soils during chemical weathering, or it may be an artefact of the low rates of ASD deposition during this period. Either way, the enrichment factors (EF) which have been presented here are conservative estimates of human impacts, compared to EFs which are calculated using crustal values for atmospheric aerosols (see below).

[34] The EF of Sb at EGR was originally calculated using Sc and the Sb/Sc ratio of the Earth's crust [*Shotyk et al.*, 1996] because the "natural background" of Sb/Sc in the peats at EGR was not yet known. Now that accurate, precise measurements of Sb have been obtained for this section of the core [*Shotyk et al.*, 2002a, 2002b] using HG-AAS [*Krachler et al.*, 2001] and confirmed using ICP-MS [*Krachler et al.*, 2002a], the "natural background" Sb concentrations (8 ng/g) and Sb/Sc ratio (0.105) are known: These values are more useful than crustal values as they provide a more realistic basis for calculating Sb enrichments not only in modern peat samples but also in plants and aerosols.

4.4. Anthropogenic Enrichments of Sb in Scottish Peat Cores

[35] The primary geochemical difference between the peat cores from Scotland and Shetland, versus those from Switzerland, is the considerable input of marine aerosols to the Scottish bogs [*Shotyk*, 1997]. Sea spray contributions of Sb to the Scottish bogs, however, would have been effectively constant over time and would not have caused a significant change in the Sb EF. The pronounced increase in Sb EF since the Industrial Revolution therefore cannot be attributed to marine inputs of Sb.

4.5. Comparison With Sb Concentrations and Sb EF in Modern Plants

[36] For comparison with the peat core data, concentrations of Sb measured in modern samples of elder and poplar leaves from Germany and South America are summarized in Tables 2 and 3, respectively. Both elder and poplar leaves collected in Germany exhibit distinctly higher Sb concentrations than the corresponding samples from remote areas of Argentina or Chile. The low Sb concentrations (4 to 5 ng/g) in the plant samples collected at remote sites from South America (Table 3) are comparable to the natural

Table 3. Concentrations (ng g^{-1} dry mass) of Sb in Virgin Poplar Leaves Collected in Autumn 1998 at Different Locations

Location	N[a]	Concentration ± s	RSD, %
Chile, Andes	3	3.9 ± 0.4	10
Argentina, lakeside	9	4.3 ± 1.3	30
Argentina, urban area	4	19.6 ± 2.3	12
Germany, industrialized area	4	131 ± 4	3.1
Germany, urban area	3	150 ± 3	2.0

[a]Number of subsamples analyzed.

background concentration of Sb from the EGR peat profile (8 ± 3 ng/g). Because Sb is not an essential element, the data presented here suggest that the ''natural background'' concentration of Sb in plants is on the order of a few ng/g and that any concentrations significantly above this may reflect an anthropogenic impact. For comparison, plant samples from urban, residential areas in Germany yield Sb concentrations that are at least 30 times higher. Even greater impacts of Sb contamination are seen in plant samples collected at sites close to vehicular traffic, i.e. motorways. Because Sb is used during the vulcanization of tires and as a fire retardant in brake shoes, there is an impressive contamination of plants by Sb emitted near roadways (Table 2). Unfortunately, there are no data about Sc concentrations in the plant materials; therefore it is not possible to correct the Sb data for dust inputs or to calculate EFs. However, we note that the ratio of Sb concentrations in urban areas versus the remote sites is remarkably similar to the maximum Sb EF seen in the peat cores.

[37] For comparison with the data published by *Krachler et al.* [1999] for vascular plants (elder and poplar leaves), we note that lichens collected in remote parts of the Northwest Territories in Canada showed Sb concentrations in the range 80 to 130 ng/g [*Puckett and Finegan*, 1980], which also are above the background levels described here by a factor of at least ten. Similarly, moss samples from southern Norway analyzed by *Steinnes* [1980] contained up to 860 ng/g Sb, compared with 70 ng/g Sb in mosses from remote northern Norway. Also, lichens from Slovenia, in central Europe, show Sb concentrations in the range 140 to 3530 ng/g [*Jeran et al.*, 1996], with the greatest Sb concentrations being found in the vicinity of lead smelters. Comparing these data and the ranges in Sb concentrations with ''background'' values, modern plant samples from diverse geographic locations appear to have been strongly impacted by anthropogenic Sb. These pronounced concentration differences support the view that the impact of human activities on the global geochemical cycle of Sb may have been underestimated by a considerable margin.

4.6. Comparison With Sb Concentrations and EF in Atmospheric Aerosols

[38] Both Sb and Sc have been measured in atmospheric aerosols by a number of authors, e.g., *Bogen* [1973], *Rahn* [1976], *Buat-Menard and Chesselet* [1979], *Maenhaut et al.* [1989], *Güllü et al.* [1996], and *Heinrichs and Brumsack* [1997]. In each case, the magnitude of the Sb EF is comparable to or greater than the values presented here for the peat cores. The data presented by *Bogen* [1973] for the city of Heidelberg, for example (Sb EF = 496) and by *Buat-Menard and Chesselet* [1979] for marine aerosols over the tropical North Atlantic (Sb EF = 250) were calculated by normalizing to crustal abundances: The EF data which we have presented here shows lower maxima partly because we have normalized to ''background'' values which are ca. 5 times greater than crustal values. Fine aerosol fractions (<2.5 μm) show even greater EF values [*Maenhaut et al.*, 1989; *Güllü et al.*, 1996]. Of all the elements studied by *Rahn* [1976], Sb showed one of the greatest ranges in EF, from a low of ca. 3.8 (Saharan dust) to a high of ca. 24,000 (Ghent, Belgium); the lowest values observed by *Rahn* [1976] are consistent with our ''background'' values, and the greatest values were found in atmospheric aerosols collected during the 1970s from highly industrialized, urban areas.

4.7. Implications for the Global Geochemical Cycle of Sb

[39] Compared with preanthropogenic values, samples from recent peats (i.e., dating from the past century) are typically enriched in Sb by 30 or 40 times, but EF up to 80 fold are seen at GDL which has been severely impacted by industrial Pb (Figure 4). These enrichments are interpreted as having been caused by the predominance of anthropogenic Sb emissions. Given the intensity of these enrichments and the fact that they extend to remote parts of NW Scotland and Shetland, it is difficult to imagine that anthropogenic emissions of Sb to the global atmosphere are comparable to natural emissions [*Pacyna and Pacyna*, 2001]. Even in remote northern Norway, the Sb concentrations in moss samples reported by *Steinnes* [1980] are still an order of magnitude greater than the ''background'' values recorded by the peat bog at EGR. In fact, the enrichments of Sb in the peat profiles described here are of a similar magnitude to those of Pb which is a truly global pollutant. Strong correlations between Sb and Pb were noted previously by Steinnes both in peat cores [*Steinnes*, 1997] and in samples of surface soil [*Steinnes et al.*, 1997].

[40] According to *Nriagu* [1990], the ratio of anthropogenic to natural emissions of Pb to the global atmosphere is 30; given the similar distributions of Sb and Pb presented here, it is reasonable to expect that human activities have impacted atmospheric Sb emissions to a similar extent. Given the phasing out of leaded gasoline which is currently taking place in most developed countries, the latest estimates of global atmospheric Pb emissions from anthropogenic sources are lower, but still a factor of ten greater than natural sources [*Pacyna and Pacyna*, 2001]. Looking again at the correlation between Sb and Pb, it is reasonable to expect that the global geochemical cycle of Sb has been impacted by human activities to the same extent as Pb.

[41] While each of the peat cores show that Sb EF values are declining, modern plant samples yield highly elevated Sb concentrations, and most atmospheric aerosols show very strong Sb enrichments, compared with ''background'' values. The plant samples studied by Krachler, for example, were collected during 1996 to 1998. Therefore if Sb enrichments really are in decline, then it may be that they are declining from very high levels. Alternatively, the spatial distribution of Sb concentrations may be subject to very pronounced Sb concentration gradients. Clearly, more detailed studies of the environmental dispersion of this element are needed, to improve our understanding of the extent of human impacts.

[42] As a result of the chemical and mineralogical association with Pb (Table 1), Sb must have been mobilized throughout human history by mining, smelting, and refining of lead ores, and lead manufacturing. According to *Hutchinson and Meema* [1987], the geochemical cycle of Pb has been impacted by human activities more than any

other metal. However, it may well be that the global geochemical cycle of Sb has been impacted to a similar extent. In fact, like Pb, most anthropogenic Sb is emitted to the atmosphere from high-temperature combustion processes which give rise to sub-micron aerosols [*Fowler and Goering*, 1991]; these have residence times of ca. 5 to 7 days, and are therefore conducive to long range atmospheric transport [*Steinnes*, 1987]. Thus like Pb, the entire Northern Hemisphere may be contaminated with anthropogenic Sb. The long history of environmental Pb pollution is well documented from polar snow and ice, lake sediments, and peat cores, and we can reasonably expect that the Sb cycle has been affected to the same extent. Additional measurements of Sb concentrations in age dated, ombrotrophic peat cores from industrial, rural, and remote areas on other continents are needed to test this hypothesis.

5. Conclusions

[43] If the natural flux of Sb recorded by the peat bog at EGR is representative of this parameter generally, and assuming that the anthropogenic fluxes published by *Nriagu* [1990] and *Pacyna and Pacyna* [2001] are correct, then the human impact on atmospheric Sb emissions has been underestimated. In fact, the anthropogenic emissions of Sb to the global atmosphere may exceed the natural fluxes by a factor of ten or more.

[44] Fluxes of trace elements from natural and anthropogenic sources to the global atmosphere are useful for highlighting the scale of human impacts. However, these comparison also have their limitations. The chemical analyses of ombrotrophic peat from central Europe indicate that the concentrations of Sb in modern peat samples (i.e., the past century) are enriched by 30 to 80 times, compared with preanthropogenic values. Given that the toxicity of Sb is comparable to that of Pb and that it too is a cumulative poison, the environmental significance of anthropogenic emissions of Sb may be comparable to that of Pb.

References

Appleby, P. G., W. Shotyk, and A. Fankhauser (1997), ^{210}Pb age dating of three peat cores in the Jura Mountains, Switzerland, *Water Air Soil Pollut.*, *100*, 223–231.

Bailey, A. R. (1961), *Textbook of Metallurgy*, 2nd ed., 561 pp., Macmillan, Old Tappan, N. J.

Bodek, I., W. J. Lyman, W. F. Reehl, and D. H. Rosenblatt (Eds.) (1988), *Environmental Inorganic Chemistry: Properties, Processes, and Estimation Methods*, Pergamon, New York.

Bogen, J. (1973), Trace elements in atmospheric aerosol in the Heidelberg area, measured by instrumental neutron activation analysis, *Atmos. Environ.*, *7*, 1117–1125.

Boyle, R. W., and I. R. Jonasson (1984), The geochemistry of Sb and its use as an indicator element in geochemical prospecting, *J. Geochem. Explor.*, *20*, 223–302.

Bränvall, M. L., R. Bindler, O. Emteryd, M. Nilsson, and I. Renberg (1997), Stable isotope and concentration records of atmospheric lead pollution in peat and lake sediments in Sweden, *Water Air Soil Pollut.*, *100*, 243–252.

Buat-Menard, P., and R. Chesselet (1979), Variable influence of the atmospheric flux on the trace metal chemistry of oceanic suspended matter, *Earth Planet. Sci. Lett.*, *42*, 399–411.

Cheburkin, A. K., and W. Shotyk (1996), An Energy-dispersive Miniprobe Multielement Analyzer (EMMA) for direct analysis of Pb and other trace elements in peats, *Fresenius J. Anal. Chem.*, *354*, 688–691.

Chen, B., M. Krachler, and W. Shotyk (2003), Determination of antimony in plant and peat samples by hydride generation-atomic fluorescence spectrometry (HG-AFS), *J. Anal. At. Spectrom.*, *18*, 1256–1262.

Crecelius, E. A., C. J. Johnson, and G. C. Hofer (1974), Contamination of soils near a copper smelter by arsenic, antimony, and lead, *Water Air Soil Pollut.*, *3*, 337–342.

Crecelius, E. A., M. H. Bothner, and R. Carpenter (1975), Geochemistries of arsenic, antimony, mercury, and related elements in sediments of Puget Sound, *Environ. Sci. Technol.*, *9*, 325–333.

Farmer, J. G., A. B. Mackenzie, C. L. Sugden, P. J. Edgar, and L. J. Eades (1997), A comparison of the historical lead pollution records in peat and freshwaer lake sediments from central Scotland, *Water Air Soil Pollut.*, *100*, 253–270.

Filella, M., N. Belzile, and Y.-W. Chen (2002a), Antimony in the environment: A review focused on natural waters, I. Occurrence, *Earth Sci. Rev.*, *57*, 125–176.

Filella, M., N. Belzile, and Y.-W. Chen (2002b), Antimony in the environment: A review focused on natural waters, II. Relevant solution chemistry, *Earth Sci. Rev.*, *59*, 265–285.

Fowler, B. A., and P. L. Goering (1991), Antimony, in *Metals and Their Compounds in the Environment*, edited by Merian, E., pp. 743–750, John Wiley, Hoboken, N. J.

Güllü, G. H., I. Ölmez, and G. Tuncel (1996), Chemical concentrations and element size distributions of aerosols in the eastern Mediterranean during strong dust storms, in *The Impact of Desert Dust Across the Mediterranean*, edited by S. Guerzoni and R. Chester, pp. 339–347, Kluwer Acad., Norwell, Mass.

Heinrichs, H., and H.-J. Brumsack (1997), Anreicherung von umweltrelevanten Metalle in atmospharisch transportierten Schwebstauben aus Ballungszentren, in *Geochemie und Umwelt*, edited by J. Matschullat, H. J. Tobschall, and V.-J. Voigt, pp. 25–36, Springer-Verlag, New York.

Jeran, Z., R. Jacimovic, F. Batic, B. Smodis, and H. T. Wolterbeek (1996), Atmospheric heavy metal pollution in Slovenia derived from results for epiphytic lichens, *Fresenius J. Anal. Chem.*, *354*, 681–687.

Kempter, H., M. Görres, and B. Frenzel (1997), Ti and Pb concentrations in rainwater-fed bogs in Europe as indicators of past anthropogenic activities, *Water Air Soil Pollut.*, *100*, 367–377.

Kimbrough, D. E., and I. H. Suffet (1995), Off-site forensic determination of airborne elemental emissions by multi-media analysis: A case study at two secondary lead smelters, *Environ. Sci. Technol.*, *29*, 2217–2221.

Krachler, M., M. Burow, and H. Emons (1999), Biomonitoring of antimony in environmental matrices from terrestrial and limnic ecosystems, *J. Environ. Monitor.*, *1*, 477–481.

Krachler, M., W. Shotyk, and H. Emons (2001), Digestion procedures for the determination of antimony and arsenic in small amounts of peat samples by hydride generation atomic absorption spectrometry, *Anal. Chim. Acta*, *432*, 303–310.

Krachler, M., H. Emons, C. Barbante, G. Cozzi, and W. Shotyk (2002a), Inter-method comparison for the determination of antimony and arsenic in peat samples, *Anal. Chim. Acta*, *458*, 387–396.

Krachler, M., C. Mohl, H. Emons, and W. Shotyk (2002b), Analytical procedures for the determination of selected trace elements in peat and plant samples by inductively coupled plasma mass spectrometery, *Spectrochim. Acta*, *B57*, 1277–1289.

Maenhaut, W., P. Cornille, J. M. Pacyna, and V. Vitols (1989), Trace element composition and origin of the atmospheric aerosol in the Norwegian Arctic, *Atmos. Environ.*, *23*, 2551–2569.

Martinez-Cortizas, A., X. Pontevedra Pomba, J. C. Novoa Munoz, and E. Garcia-Rodeja (1997), Four thousand years of atmospheric Pb, Cd, and Zn deposition recorded by the ombrotrophic peat bog of Penido Vello (northwestern Spain), *Water Air Soil Pollut.*, *100*, 387–403.

MacKenzie, A. B., J. G. Farmer, and C. L. Sugden (1997), Isotopic evidence of the relative retention and mobility of lead and radiocaesium in Scottish ombrotrophic peats, *Sci. Total Environ.*, *203*, 115–127.

MacKenzie, A. B., E. M. Logan, G. T. Cook, and I. D. Pulford (1998), Distributions, inventories, and isotopic composition of lead in ^{210}Pb-dated peat cores from contrasting biogeochemical environments: Implications for lead mobility, *Sci. Total Environ.*, *223*, 25–35.

Njåstad, O., R. Naeumann, and E. Steinnes (1987), Variations in atmospheric trace element deposition studied by INAA of peat cores from ombrotrophic bogs, *J. Radioanal. Nucl. Chem.*, *114*, 69–74.

Norton, S. A., G. C. Evans, and J. S. Kahl (1997), Comparison of Hg and Pb fluxes to hummocks and hollows of ombrotrophic Big Heath Bog and to nearby Sargent Mt. Pond, Maine, USA, *Water Air Soil Pollut.*, *100*, 271–286.

Nriagu, J. O. (1983), *Lead and Lead Poisoning in Antiquity*, John Wiley, New York.

Nriagu, J. O. (1990), Heavy metal pollution poisoning the biosphere?, *Environment*, *32*, 7–11, 28–33.

Pacyna, J. M., and E. G. Pacyna (2001), An assessment of global and regional emissions of trace metals to the atmsopherie from anthropgenic sources worldwide, *Environ. Rev.*, *9*, 269–298.

Patterson, C. C., and D. M. Settle (1987), Magnitude of the lead flux to the atmosphere from volcanoes, *Geochim. Cosmochim. Acta*, *51*, 675–681.

Puckett, K. J., and E. J. Finegan (1980), An analysis of the element content of lichens from the Northwest Territories, Canada, *Can. J. Bot.*, *58*, 2073–2089.

Rahn, K. A. (1976), The chemical composition of the atmospheric aerosol, technical report, 265 pp., Grad. Sch. of Oceanogr., Univ. of R. I., Kingston.

Shotyk, W. (1996), Peat bog archives of atmospheric metal deposition: Geochemical assessment of peat profiles, natural variations in metal concentrations, and metal enrichment factors, *Environ. Rev.*, *4*, 149–183.

Shotyk, W. (1997), Atmospheric deposition and geochemical mass balance of major elements and trace elements in two oceanic blanket bogs, northern Scotland and the Shetland Islands, *Chem. Geol.*, *138*, 55–72.

Shotyk, W., A. K. Cheburkin, P. G. Appleby, A. Fankhauser, and J. D. Kramers (1996), Two thousand years of atmospheric arsenic, antimony, and lead deposition recorded in a peat bog profile, Jura Mountains, Switzerland, *Earth Planet. Sci. Lett.*, *145*, E1.

Shotyk, W., A. K. Cheburkin, P. G. Appleby, A. Fankhauser, and J. D. Kramers (1997), Lead in three peat bog profiles, Jura Mountains, Switzerland: Enrichment factors, isotropic composition, and chronology of atmospheric deposition, *Water Air Soil Pollut.*, *100*, 297–310.

Shotyk, W., D. Weiss, P. G. Appleby, A. K. Cheburkin, R. Frei, M. Gloor, J. D. Kramers, S. Reese, and W. O. van der Knaap (1998), History of atmospheric lead deposition since 12,370 ^{14}C yr BP recorded in a peat bog profile, Jura Mountains, Switzerland, *Science*, *281*, 1635–1640.

Shotyk, W., P. Blaser, A. Grünig, and A. K. Cheburkin (2000), A new approach for quantifying cumulative, anthropogenic, atmospheric lead deposition using peat cores from bogs: Pb in eight Swiss peat bog profiles, *Sci. Total Environ.*, *249*, 257–280.

Shotyk, W., D. Weiss, J. D. Kramers, R. Frei, A. K. Cheburkin, M. Gloor, and S. Reese (2001), Geochemistry of the peat bog at Etang de la Gruère, Jura Mountains, Switzerland, and its record of atmospheric Pb and lithogenic trace elements (Sc, Ti, Y, Zr, Hf and REE) since 12,370 ^{14}C yr BP, *Geochim. Cosmochim. Acta*, *65*, 2337–2360.

Shotyk, W., D. Weiss, M. Heisterkamp, A. K. Cheburkin, and F. C. Adams (2002a), A new peat bog record of atmospheric lead pollution in Switzerland: Pb concentrations, enrichment factors, isotopic composition, and organolead species, *Environ. Sci. Technol.*, *36*, 3893–3900.

Shotyk, W., M. Krachler, A. Martinez-Cortizas, A. K. Cheburkin, and H. Emons (2002b), A peat bog record of natural, pre-anthropogenic enrichments of trace elements in atmospheric aerosols since 12,370 ^{14}C yr BP, and their variation with Holocene climate change, *Earth Planet. Sci. Lett.*, *199*, 21–37.

Shotyk, W., M. E. Goodsite, F. Roos-Barraclough, J. Heinemeier, R. Frei, G. Asmund, C. Lohse, and T. H. Stroyer (2003), Anthropogenic contributions to atmospheric Hg, Pb, and As deposition recorded by peat cores from Greenland and Denmark dated using the ^{14}C ams "bomb pulse curve", *Geochim. Cosmochim. Acta*, *67*, 3991–4011.

Steinnes, E. (1980), Atmospheric deposition of heavy metals in Norway studied by the analysis of moss samples using neutron activation analysis and atomic absorption spectrometry, *J. Radionanal. Chem.*, *58*, 387–391.

Steinnes, E. (1987), Impact of long-range atmospheric transport of heavy metals to the terrestrial environment in Norway, in *Lead, Mercury, Cadmium and Arsenic in the Environment*, edited by T. C. Hutchinson and K. M. Meema, pp. 107–117, John Wiley, Hoboken, N. J.

Steinnes, E. (1997), Trace element profiles in ombrogenous peat cores from Norway: Evidence of long range atmospheric transport, *Water Air Soil Pollut.*, *100*, 405–413.

Steinnes, E., and O. Njåstad (1995), Ombrotrophic peat bogs as monitors of trends in atmospheric deposition of pollutants: Role of neutron activation in studies of peat samples, *J. Radioanal. Nucl. Chem.*, *192*, 205–213.

Steinnes, E., R. O. Allen, H. M. Petersen, J. P. Rambæk, and P. Varskog (1997), Evidence of large scale heavy-metal contamination of natural surface soils in Norway from long range atmospheric transport, *Sci. Total Environ.*, *205*, 255–266.

Vile, M. A., M. J. Novak, E. Brizova, R. K. Wieder, and W. R. Schell (1995), Historical rates of atmospheric Pb deposition using ^{210}Pb dated peat cores: Corroboration, computation, and interpretation, *Water Air Soil Pollut.*, *79*, 89–106.

Vile, M. A., R. K. Wieder, and M. Novak (1999), Mobility of Pb in Sphagnum-derived peat, *Biogeochemistry*, *45*, 35–52.

Weiss, D., W. Shotyk, P. G. Appleby, A. K. Cheburkin, and J. D. Kramers (1999a), Atmospheric Pb deposition since the Industrial Revolution recorded by five Swiss peat profiles: Enrichment factors, fluxes, isotopic compositon, and sources, *Environ. Sci. Technol.*, *33*, 1340–1352.

Weiss, D., W. Shotyk, M. Gloor, and J. D. Kramers (1999b), Herbarium specimens of Sphagnum moss as archives of recent and past atmospheric Pb deposition in Switzerland: Isotopic composition and source assessment, *Atmos. Environ.*, *33*, 3751–3763.

B. Chen, M. Krachler, and W. Shotyk, Institute of Environmental Geochemistry, University of Heidelberg, INF 236, D-69120 Heidelberg, Germany. (b.chen@ugc.uni-heidelberg.de; krachler@ugc.uni-heidelberg.de; shotyk@ugc.uni-heidelberg.de)